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Silanol dyes for solar cells: higher efficiency and significant durability

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Azobenzene-containing silanol dyes were synthesized, and their applicability to dye-sensitized solar cells was investigated. Silanol dyes showed better effectiveness when compared with conventional carboxy-substituted azobenzene dyes. Moreover, silanol dyes showed better durability than carboxyl dyes; ~90% of silanol dyes remained intact on the TiO₂ electrode of the solar cell after being immersed in water for 96 h, whereas in the case of carboxy dyes this figure was less than 20%. Copyright © 2010 John Wiley & Sons, Ltd.

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Introduction

The energy conversion efficiencies of dye-sensitized solar cells (DSSCs) are approaching 12% after Grätzel's development of the nanocrystalline cell.^[1,2] However, in the last decade, the improvement in the energy conversion efficiency has been less than 1%, indicating that new materials are necessary to realize 15% efficiency for application. In recent applications of DSSCs, another problem has been encountered, namely durability. The existing sensitizing dyes contain sulfonic, phosphonic or carboxy groups bound to TiO₂;^[3,4] these bonds are susceptible to hydrolysis, which affects the lifespan of the dye. This is a serious problem because a shorter lifespan has a direct impact on the total cost. Moreover, tight sealing is required for preventing water from penetrating the device. In order to find a solution to these problems, we examined the use of silanols for dye-sensitized solar cells. In earlier studies, we had reported the versatility of silanols as starting compounds for cage siloxanes^[5-8] and laddersiloxanes,^[8,9-12] or as host molecules.^[13-15] We had also proved that silanols form very strong bonds with most metal oxides such as alumina, titania or silica.^[16] Further, addition of silicon atoms to a π -system enhances electron delocalization - a bathochromic shift and hyperchromic effect are observed in most cases.^[17] These two strong points prompted us to develop silanol dyes for solar cells. In this paper, we describe the introduction of silicon atoms to dyes and the impact on the effectiveness and durability of solar cells.

Results and Discussions

Synthesis of Silanol Dyes

Our first approach involved the transformation of the carboxy group to silyl substituents. Through this approach, a substantial number of dyes with carboxyl groups can be utilized as starting compounds. We used benzoic acid or salicylic acid as model compounds and examined their reaction with various chlorosilanes. Unfortunately, we could not obtain the target compounds in the reaction conditions that we used. We used gas chromatography (GC) to trace the reaction, and we observed



Scheme 1. Bonding schemes of carboxylic acid.

that the starting materials were consumed without any problem. Therefore, we hypothesize that the target compounds could not be obtained because of the instability of silyl esters of carboxylic acids. During the procedure of purification (using column chromatography or distillation), silyl esters underwent decomposition, which indicates that they were unstable in the presence of moisture. These results clearly indicate that the bond between carboxyl acid and silanol is not stable. Since the nature of the bonding between carboxylic acid and silanol or titanol is similar, the chemical bonding of carboxylic acid with titanium oxide is also expected to be weak and liable to hydrolysis (Scheme 1). In order to establish the durability of solar cells, anchor point substituents must be carefully chosen; conventional carboxy groups may not serve the purpose.

Since the method of modification of carboxylic dyes did not work, we then considered the introduction of silyl groups into the dyes. With this modification, electron delocalization brings

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Scheme 2. Preparation of azobenzene-substituted silanols.



Figure 1. UV–vis absorption spectra of **2**, **3** and azobenzene in acetonitrile solutions: the solid line represents the result for **2**, the broken line that for **3** and the dotted line azobenzene.

about bathochromic shift and hyperchromic effect. Both these are favorable for solar cell dyes.

Admittedly, azobenzene is not the best sensitizer for a solar cell; however, easy access to azobenzene-substituted silanol is advantageous for the comparison of electronic properties and stability of silanol and carboxylic acid dyes. Moreover, the fact that azobenzene has a simple formula makes the orbital calculations easier. Therefore, we then tried to synthesize silylazobenzene. All attempts at the preparation of 4-phenylazosilanetriol (1) failed, probably because of the decomposition of triols by condensation. On the other hand, the synthesis of bis(4phenylazophenyl)silanediol (2) proceeded well and we obtained the product as an orange-yellow solid that was stable in both air and moisture (Scheme 2). The UV-vis spectra of azobenzene derivatives are summarized in Fig. 1. While the absorption of 4carboxyazobenzene 3 is similar to that of azobenzene, the effect of silyl substituents of 2 is noticeable. Notably, the absorption coefficient of 2 is 2.3 times higher than that of 3 in the visible light region of $\lambda = 445$ nm. Thus, silanol dye **2** is clearly useful for DSSCs. The results of the UV-vis spectra of the silvl derivatives in solution are summarized in Table 1.

Effectiveness of Silanol Dyes as a Sensitizer for Solar Cells

The silanol dye **2** was observed to work as a sensitizer in a dyesensitized solar cell (DSSC), as reported shortly in our previous paper.^[18] In this work, we measured the I-V properties of the cells using **2** and **3** as sensitizing dyes to obtain a precise and

Table 1. Summary of UV-vis spectra in acetonitrile solutions				
Compounds	bounds λ_{max} , nm (ε)			
Azobenzene 2 3	440 (530), 316 (20500), 227 (13000) 445 (1480), 323 (46900), 229 (24900) 444 (650), 322 (22900), 228 (10500)			

quantitative comparison of sensitizing properties between the dyes containing silanol and carboxy groups. Figure 2 shows the absorption spectra in visible-light region of 2 and 3 adsorbed on the TiO_2 electrodes, which were used in the cells for I-Vmeasurements. The spectra were obtained by subtracting the absorption due to the TiO₂ electrode from those of dye-adsorbed TiO₂ electrodes. From these spectra, the relative values of difference absorbance at the absorption maxima were estimated to be 0.125 for 3 and 0.153 for 2. In the wavelength region the ε value of **2** in solution is about 2.3 times larger than that of **3**, thus we could estimate the relative amount of the molecules of 3 adsorbed on TiO₂ electrode to that of **2** to be 1.9:1. As compound 2 has two azobenzene moieties per molecule, the total number of azobenzene moieties on the electrode surfaces is considered to be fairly close between the cases of 2 and 3. Thus, we can safely assume that the number of azobenzene moieties on the device is the same for **2** and **3**, and that direct comparison of I - V properties is possible. The result of the I-V measurement is shown in Fig. 3. The cells containing **2** exhibited higher short-circuit current (J_{sc}) values than the cells containing **3** or the cells containing no dye. As a result, the light-to-electric energy conversion efficiency (η) of the cells with 2 is higher than that of the cells with 3 by a factor of 2.7 under the present test conditions. The results of the measurement are summarized in Table 2. These results reveal that 2 is effective as a sensitizing dye for DSSCs. They also prove that electron transfer from the light-excited dye to the TiO₂ electrode of 2 through the Si-O-Ti bonds is more efficient than that of 3 through the ester-like bond.

Durability of Silanols Dyes

In the case of solar cells with conventional carboxy dyes, instability of the dye-adsorbed electrodes to water is a major problem. In order to prevent ingress of moisture, tight sealing is necessary, and even after this, effectiveness decreases after some time. This instability is based on the weakness of the ester-like bond formed



Figure 2. UV-vis absorption spectra of ${\bf 2}$ and ${\bf 3}$ adsorbed on TiO_2 electrodes: the solid line represents the result for ${\bf 2}$ and the broken line 3.



Figure 3. I-V properties of the cells using **2** and **3** as sensitizing dyes and that without dye under a simulated sunlight irradiation: the solid line represents the result for **2**, the broken line that for **3** and the dotted line without dye.

Table 2. I-V properties of the cells using 2 and 3 as sensitizing dyesand with no dye					
Dyes	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}$ (V)	FF	η (%)	
3	0.715	0.492	0.433	0.152	
2 With no dye	1.674 0.307	0.513 0.408	0.485 0.411	0.416 0.0515	

between the dye and the TiO₂ electrode. In the case of silanol dyes, on the other hand, the chemical adsorption of the dye to the TiO₂ electrode is performed by the formation of a Si–O–Ti bond between the silanol moiety of the dye and the TiO₂ electrode, and the formed Si–O–Ti bond is expected to be much more stable than the ester-like bond. To check the durability, we soaked the dyes on TiO₂ in water at 25 °C, and measured the change of the absorption at $\lambda = 414$ nm (see Fig. 2). As shown in Fig. 4, carboxy



Figure 4. Changes of the absorptions due to the dyes **2** and **3** adsorbed on the TiO₂ electrodes with the soaking time in water at 25 °C: open circles represent the results for **2** and solid circles that for **3**. The absorption ratios were evaluated by the normalization of absorbance at $\lambda = 414$ nm with respect to those before soaking in water.

dye **3** lost more than 80% of its volume after 96 h, while silanol dye **2** retained about 90% of its volume. This property of silanol dyes of bonding tightly to the TiO_2 electrode could be a great advantage in the utilization of silanol dyes as sensitizing dyes for DSSCs.

These results clearly indicate that silanol dyes are promising from the viewpoints of both higher effectiveness of electron transfer as well as durability.

Conclusion

The results of our investigation of alternative compounds for practical application in dye-sensitized solar cells can be summarized as follows: (1) introduction of silyl groups into dyes resulted in bathochromic shift and higher absorption coefficient; (2) transformation of known dyes with carboxylic groups to silanols or alkoxysilanes was unsuccessful; (3) silanol dyes showed better effectiveness and durability than carboxyl dyes.

We are currently investigating more effective variants of silanol dyes as well as the quantitative comparison of the durability of dyes for solar cells.

Experimental

The reactions were carried out under either an argon or a nitrogen atmosphere. Fourier transform nuclear magnetic resonance spectra were obtained using a Jeol model AL-300 (¹H at 300.00 MHz) and Jeol model α -500 (¹H at 500.00 MHz, ¹³C 125.65 MHz, ²⁹Si at 99.25 MHz). Chemical shifts were reported as δ units (ppm) relative to SiMe₄, and residual solvent peaks were used for standards. For ²⁹Si NMR, SiMe₄ was used as an external standard. Electron ionization mass spectrometry was performed with a Jeol JMS-DX302 and JMS-700. Electrospray ionization mass spectra (ESI-MS) were recorded on an Applied Biosystems/MDS-Sciex API-100 spectrometer. Infrared spectra were measured with a Shimadzu FTIR-8700. UV – vis spectra were recorded on a Hitachi U-3010 spectrometer, and an integrating sphere was equipped to the spectrometer for the measurements of the dyes adsorbed on the TiO₂ electrodes.

Synthesis of bis(4-Phenylazophenyl)silanediol (2)

Butyl lithium (0.70 mmol, hexane solution) was added to a solution of 200 mg (0.649 mmol) of 4-iodoazobenzene^[19] in

20 ml of Et₂O under stirring at -70 to -20 °C. After 1 h, 72 mg (0.47 mmol) of tetrachlorosilane was added at the same temperature and stirred for 17 h. The resulting solution was washed three times with 20 ml of brine and evaporated. The residue was recrystallized from hexane – ether to yield 56 mg (20%) of bis(4-phenylazophenyl)silanediol as an orange-red powder. M.p. 154.2 – 157.9 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.20 (m, 1H), 7.45 (m, 3H), 7.70–7.95 (m, 5H). ¹³C NMR (125.65 MHz, CDCl₃) δ 22.3, 122.4, 123.1, 129.2, 131.3, 136.2, 152.7, 154.0 ppm. ²⁹Si NMR (99.25 MHz, CDCl₃) δ –21.8 ppm. IR (KBr, cm⁻¹) ν 323, 3065, 1593, 1385, 1120, 1074, 835, 766, 685, 598, 554. MS *m/z* (%) 423 (100), 259 (50). Anal. calcd for C₂₄H₂₀N₄O₂Si: C, 67.96; H, 4.75; N, 13.21. Found: C, 68.66; H, 4.49; N, 13.32.

Preparation of a Solar Cell

The nanocrystalline TiO₂ film electrodes were prepared by spincoating TiO₂ paste on an F-doped SnO₂ (FTO) coated glass plate (25 × 50 mm², 15–20 Ω/sq; Asahi Glass) followed by sintering of the TiO₂ layer at 450 °C for 30 min, and then by spin-coating the TiO₂ paste again and sintering it at 500 °C for 30 min. The TiO₂ paste was prepared by mixing P-25 (Nippon Aerosil) TiO₂ particles with water, acetylacetone and Triton X-100 and grinding them in an agate mortar. The thickness of the TiO₂ films with porosity was estimated to be ~2.1 µm by SEM observation of the cross section of the TiO₂ electrode. Adsorption of the sensitizing dyes on the TiO₂ electrodes was performed by immersing the electrode in the 3.0×10^{-4} M toluene solutions of dyes at 100 °C for 15 h.

Photovoltaic Measurement

The photovoltaic measurements were performed for the electrochemical cell consisting of a dye-adsorbed TiO₂ electrode, a counter electrode, a polyethylene film spacer (100 µm thick), and an organic electrolyte. A Pt-sputtered FTO-coated glass plate was used as the counter electrode, and a solution of 0.3 M Lil and 0.015 M l₂ in acetonitrile–ethylene carbonate (2:8 in volume) was used as the electrolyte. The photovoltaic performance of the solar cells was assessed from the *I*–*V* properties of the cells measured with a solar simulator of OTENTO-SUN III (Bunkoh-Keiki) and a source meter of R6240A (Advantest). The aperture area of the cells was maintained at 1.0 cm² using a shading mask and the *I*–*V* properties were measured under irradiation of AM-1.5G global-one sun condition (100 mW cm⁻²) at 25 \pm 2°C.

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